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The Controlled Oxidation of Leonardite

Vijay R. Purandare

THE CONTROLLED OXIDATION OF LEONARDITE

by

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This thesis, submitted by Vijay Purandare in partial fulfillment of the requirements for the Degree of Master of Science in the University of North Dakota, is hereby approved by the Committee under whom the work has been done.

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Vijay R. Purandare, Master of Science

The controlled oxidation of dissolved leonardite was carried out in a heated autoclave under elevated oxygen pressure. Oxidation was carried out in order to increase the acidity of leonardite and obtain higher humic acid yields. The solvent was an aqueous solution of sodium hydroxide in the range of concentrations from 1% to 8%. The reaction temperature was varied from 25°C to 125°C; the pressure was kept at 500 psig and reaction time was constant at one hour. The product was analyzed both for carboxylic acid and for hydroxyl groups.

The increase in carboxyl and hydroxyl groups was slight under the optimum reaction conditions studied. The optimum conditons were: for temperature, between 50°C and 75°C, and for concentration, between 2% and 6%. However at the 4% caustic concentration level, there was no increase in carboxyl and hydroxyl groups between 50°C and 75°C. Higher temperatures and higher concentrations of caustic resulted in lower yields of humic acids either because decarboxylation occurred or because the acids became water soluble.

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INTRODUCTION

The broad objective of this research was to increase the humic acid content of leonardite and improve yields. Leonardite is a coal-like substance similar in structure and appearance to lignite coal and is believed to be derived from lignite by natural oxidation. The investigation was designed to develop the optimum conditions required for the oxidation of leonardite to higher yields and increased acidity of the humic acids produced.

The term humic acid refers to the caustic-soluble portion of coals and soils. In general, humic acids are not chemically uniform substances but are hydrophilic, reversible colloids with molecular weights varying from 300 to as high as 10,000.(25) They are described as polycarboxylic acids linked together by ether linkages.(14) The humic acids which are naturally present in good soil are partly responsible for nitrogen fixation and help make soil nutrients available to the plant by improving the physical structure of the soil. It has been shown that humic acids improve plant yields and decrease loss of moisture from the soil.

The humic acids are dark brown to black, amorphous, non-volatile, infusible and water insoluble substances. The sodium salts

are soluble in water but insoluble in alcohol and have low equivalent weights when dissolved in suitable organic solvents. (11)

The main problem attacked in this work is that of adding oxygen to suitable sites in the humic acid molecules present in leonardite and thus increasing the acidity and percent yield of caustic soluble material. The oxidation of leonardite was carried out in aqueous sodium hydroxide solutions.

BACKGROUND

Considerable research on the controlled oxidation of coal has been described in the literature. In each case the main aim was to obtain valuable chemicals including organic acids. Coals of low rank may be oxidized to form organic acids with less difficulty than coals of high rank. (6) Hence low rank coals may be considered as potentially valuable raw materials for the production of organic acids.

The United States of America and in particular, North Dakota, has numerous deposits of leonardite. The leonardite contains about 30% oxygen on a moisture free basis as compared to 20% oxygen for lignite. (18) Table 1 gives a typical analysis of leonardite and lignite.

The term leonardite is little known outside lignite producing areas of the North Central states, since leonardite has been developed commercially only to a minor extent. The higher oxygen content and less compact structure of leonardite compared with lignite make leonardite less desirable as a fuel. However, because of these characteristics, it has potential as a source of organic chemicals. The higher oxygen content of leonardite is due entirely to a larger number of carboxylic acid and hydroxyl groups. This explains the high solubility of leonardite in alkaline solution. Spectral studies indicate that the

TABLE 1

TYPICAL ANALYSES OF LIGNITE AND LEONARDITE

	Leonardite Percent	Lignite Percent
Proximate (as received):		
Moisture	42.6	36.2
Volatile Matter	26.4	26.4
Fixed Carbon	22.6	31.0
Ash	8.4	6.4
Ultimate (m.a.f.):		
Hydrogen	3.7	5.1
Carbon	65.7	73.8
Nitrogen	1.3	1.2
Oxygen (Difference)	28.4	19.9
Sulphur	0.9	1.0

material is largely composed of mixed salts of humic acids.

The present usage of leonardite is limited and its present production small as compared to lignite. It is used as a dispersant and for viscosity control in oil-well drilling muds. It is also used as a stabilizer for ion-exchange resins in water treatment. Recently, leonardite has been proposed as a potential binding material for taconite ore. Leonardite is used as a soil conditioner for replenishing the depleted humic acids of soils.(3, 25) Attempts are being made to produce nitrogen-enriched humic acid by the ammoniation of leonardite. Recent investigations have indicated that these products perform as well as conventional fertilizers and release nitrogen more slowly.(25)

The controlled oxidation of coal has been investigated by many workers in order to obtain higher yields of humic acid. However, in order that oxidation be commercially feasible, the reagents used must be cheap and readily available, as the end products must compete with relatively low cost materials. The large number of products formed make it difficult to obtain pure chemicals. The most economical oxidizing agent is air but other reagents such as nitric acid, pure oxygen, chlorine and potassium permanganate have been used in previous work.(11, 15)

An outline of previous work on different coals in different solvents and with different oxidizing agents is given in the following pages.

One of the most difficult parts of the oxidation process is

solubilizing coal in a suitable medium. A slurry cannot be used as oxygen cannot reach active sites because of the large size of particles. In a recent paper by Van Krevelen(26) it was shown that solubility of coals in organic solvents in general decreases with increasing coalification. Van Krevelen predicted that pyridine and ethylene diamine would be very good solvents for solubilizing coals of high rank. At higher temperature, phenanthrene and higher condensed aromatic substances (pitch) would be good solvents. Coals in general become more soluble after oxidative reaction. Solvent extraction of nitro humic acids from oxidation of bituminous coals by nitric acid is reported by Polansky and Kinney(16). A 90% acetone solution extracts about 85% of the nitrohumic acids formed from bituminous coal. In addition to acetone other solvents were also listed.

After leonardite is washed with dilute hydrochloric acid, it readily dissolves in acetone, dimethylacetamide, dimethylformamide and pyridine. The humic acids from leonardite can be brought in aqueous solution by increasing the pH by means of alkali. Calcium hydroxide is ineffective however, because of the reaction between calcium ions and humic acids, in which insoluble calcium humates are formed.

Oxidation of coals by air has been extensively studied and promoters such as vanadates and nitrates have been recommended.(1, 8, 10) Some workers have used fluidization techniques for oxidation.(19) The main drawback of these processes is lack of control over oxidation.

Oxidation can be controlled at lower temperatures but reaction times up to several days are required.(1, 5, 6, 8) Quick oxidation can be achieved at higher temperatures but large amounts of carbon dioxide are produced. Hence air has proved to be an unsuitable agent for the oxidation of coals.

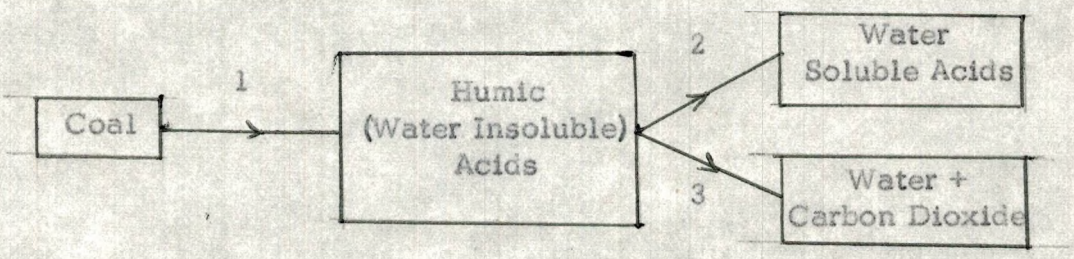
In general, bituminous coals react with oxygen to form -COOH, -OH and -C = O groups. The exact percentage of oxygen in the form of these functional groups depends on the rank of coals as well as the temperature and duration of reaction. Normally the aromatic nuclei of the humic acids formed are stable at relatively low temperatures. A relatively small number of nuclei make up the bulk of the hydrocarbon portion of the acids. Only eight nuclei make up more than 94% by weight of total acid.(14) The main constituents are methyl naphthalene, benzene and biphenyl for the acids obtained by the alkali-oxygen oxidation of bituminous coal.

A process for the oxidation of coal by nitric acid to produce nitro-humic acid has been patented by a Japanese firm.(7) A suspension of pulverized coal and dilute nitric acid is passed through at least three zones all maintained at optimum temperatures between 40°C and 100°C. The product is used as a soil conditioner. It is possible to use nitro-humic acid as a fertilizer by increasing the nitrogen content.(25) Nitric acid appears to be the least expensive reagent other than air or oxygen. The controlled oxidation of peat with nitric acid has been

described by Piret.(15) The main objection to nitric acid, however is that too many nitro groups are introduced into the humic acids and that the control of the oxidation is difficult.

Potassium permanganate oxidation is too drastic for the production of humic acids and results in the production of water soluble acid and large amounts of carbon dioxide. Oxygen has been recommended as one of the best oxidizing agents for quick and controlled oxidation. Since bituminous coal dissolves in hot sodium hydroxide solution, work has been done using sodium hydroxide as a digesting medium for subsequent oxidation.(4, 13, 21, 22, 23) Temperatures ranged from 200°C to 350°C and pressures up to 1000 psig were used with reaction times up to several hours. About 50% of the carbon was converted to carbon dioxide. Large amounts of sodium carbonate were formed. It has been recommended that continuous reactors would be more efficient than batch reactors.(10, 13)

The mechanism of formation of aromatic carboxylic acids from coal by oxygen oxidation in alkaline medium can be represented by the following schematic diagram:



As stated earlier the humic acid content of leonardite is high and therefore, it is likely to contain more active sites for further oxidation than lignite. It was decided to oxidize leonardite under controlled conditions. Oxidation was carried out to the extent that acidity of humic acids increased to a maximum value. As shown in the diagram, an attempt was made to achieve stage number one. Stages two and three take place simultaneously. Further exposure to heat and oxygen results in decarboxylation of humic acids to form carbon dioxide and water or in water soluble acids.(4, 20, 21, 22, 23)

PRELIMINARY STUDIES

A) Solubility Studies

As it was desirable to solubilize leonardite before oxidizing it, attempts were made initially to find a suitable solvent. Preliminary work on the solubility of leonardite showed that it is practically insoluble in most of the common organic solvents including acetone. The very low solubility of leonardite in organic solvents is probably due to its high calcium content. Calcium ties up most of the macromolecules of humic acids as calcium humate which is insoluble in common organic solvents.

Work was done on sodium hydroxide as a solvent for leonardite. When leonardite dissolved in aqueous sodium hydroxide solution, a colloidal dispersion rather than a true solution was obtained. This solution did not filter even through a gooch crucible. Thus centrifugation was employed to separate the insolubles.

Following the initial work with sodium hydroxide, the following procedure was adopted to determine the solubility of leonardite in a given solvent. A known weight of leonardite was added to a beaker containing a specified volume of solvent. A magnetic stirrer was used for mixing. After a certain length of time, the slurry was centrifuged

and clear filtrate was decanted to a watch glass. The solvent was evaporated in a hood until the extracted portion appeared dry. This product was heated in the oven at 105°C for one hour and weighed. The solubility was calculated as the fraction extracted by the solvent of the original weight of leonardite (MAF).

This procedure showed that leonardite dissolves more readily in 1% and 2% concentrations of sodium hydroxide than at higher concentrations at the solvent solute ratio considered. At higher concentrations the powdered leonardite has a tendency to lump together. The main reason why leonardite dissolves in an aqueous sodium hydroxide is that the sodium humate formed dissolves in water whereas calcium humates and humic acids are insoluble in water. It was possible to extract about 71% of leonardite (moisture free) using 2% aqueous solution of sodium hydroxide.

Further studies were done on solubilities of raw leonardite using various organic solvents at room temperatures. In the case of acetone, the solubility was negligible. Other solvents used were dimethylacetamide, dimethylformamide and pyridine. In each case, no appreciable solubility was observed.

Further solubilities were determined for leonardite which had been washed with dilute hydrochloric acid. Washing with hydrochloric acid removes some of the minerals, e.g. calcium and magnesium, which are partly responsible for the insolubility of leonardite. A 90% acetone-water mixture extracted about 75% of acid-washed leonardite (moisture

free basis).

For the solvents dimethylacetamide and dimethylformamide, the following procedure was adopted. One gram of acid washed leonardite was placed into a beaker and 15 ml. of solvent was added. The mixture was stirred for 30 minutes at room temperature and then centrifuged for 10 minutes. The clear filtrate was decanted and evaporated to dryness in a hood. It was further dried in the oven at 105°C and weighed. The solubility was calculated as a fraction of the original leonardite (moisture free basis). The solubility of leonardite in dimethylacetamide was observed to be 97.7% (moisture free basis) and in dimethylformamide 93.7% (moisture free basis).

The solubilities are tabulated in Table 2.

In spite of the high solubilities of leonardite in dimethylacetamide and dimethylformamide, these solvents were not used in oxidation of leonardite because they are unstable at elevated temperatures and high oxygen pressures. It is desirable to use excess oxygen for good oxidation.(13) As aqueous sodium hydroxide dissolves about 72% (moisture free) of leonardite, it was decided to use various concentrations of sodium hydroxide for oxidation of leonardite.

B) Oxidation Studies

Preliminary plans were to use 5%, 10%, 15% and 25% solutions of sodium hydroxide for oxidizing leonardite. These concentrations were

TABLE 2

SOLUBILITY OF LEONARDITE AT ROOM TEMPERATURE

Type of Leonardite	Solvent	Percentage Solubility (moisture free basis)
Raw Leonardite	2% Aqueous solution of sodium hydroxide	72%
Acid Washed Leonardite	90% Acetone - water mixture	75%
Acid Washed Leonardite	Dimethylacetamide	97.7%
Acid Washed Leonardite	Dimethylformamide	93.7%

selected since they cover the range used by Montgomery and McMurtie (13) to oxidize bituminous coal. The temperature was to be varied from 100°C to 250°C with intervals of 50°C and pressure from 200 psig to 800 psig with intervals of 200 psig. The duration of the run was to be varied from 10 minutes to 25 minutes with intervals of five minutes. However, it was found that the concentrations of sodium hydroxide used in the reaction were too high for the controlled carboxylation of leonardite as proved by low humic acid yields. Higher temperature also favored, probably, the decarboxylation of humic acids in leonardite to carbon dioxide and water, and the production of water-soluble acids over the carboxylation of the aromatic or olefinic structures in leonardite. Results of these runs are shown in Appendix E.

Therefore, a new milder design was adopted with concentration levels of 1%, 2%, 6% and 8% of aqueous solutions of sodium hydroxide. Four levels of temperature were chosen: 25°C, 50°C, 75°C and 125°C. From the initial studies it was found the pressure above 500 psig did not have an appreciable effect on the course of the reaction and hence pressure was maintained at 500 psig throughout. The duration of the reaction was extended to one hour to complete the reaction. In the runs, the temperature history showed that temperature levelled off after 30 minutes thus indicating that the reaction was completed.

EXPERIMENTAL PROCEDURE

A complete procedure for sample preparation is given in Appendix A. A 25 gram sample of leonardite was slowly added to a one liter beaker containing 500 milliliters of sodium hydroxide solution of desired concentration and stirred. Precautions were taken to see that all the leonardite became dispersed.

The slurry of leonardite in sodium hydroxide was poured into a one-liter autoclave, Parr Series 4500, provided with a paddle stirrer. The autoclave was sealed and the stirrer started. Then the autoclave was heated to the desired temperature in 40 to 50 minutes and finally pressurized with commerical oxygen. The temperature history of the reactor was recorded and the pressure inside the autoclave maintained at 500 psig. The reaction was continued for one hour.

It was difficult to heat the reactants in the vessel to a preselected temperature because of temperature lag in the apparatus. This was mainly due to the air gap between the furnace and the reactor. This problem was solved to a certain extent by setting the variable transformer to a certain predetermined position and then allowing the furnace to warm up. Then the reactor was placed in the furnace and the temperature history was recorded. As the desired temperature was approached,

heating was gradually reduced and when the desired temperature was attained, heating was stopped. This method gave desired temperatures with an accuracy of $\pm 6^{o}$. During the course of the reaction it was observed that temperature rose initially for about twenty five minutes and then started to decrease. As the temperature dropped below the desired temperature, heating was resumed by adjusting the variable transformer to maintain the temperature at a desired value.

A complete temperature history and sample calculation for a typical run is given in Appendix B.

The slurry in the autoclave was sampled after one hour through a sampling valve. The first 25 grams of slurry were discarded to clear the line and then approximately 25 grams of slurry were collected in a 250 ml. erlenmeyer flask. Three 25 grams samples were collected in this manner. After being cooled the samples were weighed to 0.1 gram.

Early attempts at product sampling through the sampling valve had met with losses due to foaming. Great care was needed to make sure that no product spurted out of the sample receiving flask. Satisfactory operation was achieved by opening the sample valve very slowly.

ANALYTICAL PROCEDURE

The sample of oxidized product was centrifuged for exactly five minutes to remove undissolved and suspended material. The clear filtrate was then decanted into a beaker. The residue in the centrifuge tube was washed twice with about five milliliters of water and washings were added to the filtrate. The filtrate was then made slightly acidic with concentrated hydrochloric acid to precipitate humic acids. Care was taken not to add too much excess hydrochloric acid because this would cause peptization in filtration later. The humic acid precipitate was then dried on a hot plate until no further fumes of hydrochloric acid were observed.

The humic acid was washed with very dilute hydrochloric acid to remove any sodium chloride formed in the reaction between hydrochloric acid and sodium carbonate. Distilled water could not be used because repeated washing with distilled water causes redispersion of the humic acid. The filter paper was dried in an oven for 15 minutes and the humic acid transferred to a tared crucible and heated for one hour at 105°C to remove all moisture, cooled and weighed. The yield of humic acid was then calculated.

Previous investigators determined the total acidity of humic acids

by treatment with an aqueous solution of sodium hydroxide and then back titrating with a standard solution of hydrochloric acid.(6) This method could not be used on the product from leonardite oxidation because of the high calcium content of the original leonardite. Calcium humate will react with sodium hydroxide to form sodium humate and calcium hydroxide.

$$Ca(Hm)_2 + 2NaOH \longrightarrow 2NaHm + Ca(OH)_2$$

The calcium hydroxide thus formed will interfere with the back titration of sodium hydroxide by hydrochloric acid. Another drawback of the former procedure was that the colloidal dispersion of leonardite in sodium hydroxide could not be filtered and the end point of the titration was not clear.

The following procedure was adopted to overcome these difficulties. The humic acid was transferred to a 125 ml. erlenmeyer flask and 50 ml. of $\frac{N}{5}$ alcoholic sodium hydroxide was added. The mixture was refluxed on a water bath for 30 minutes. A water condenser was provided so that no alcohol escaped during the refluxing. The sodium humate which was formed was insoluble in alcohol and precipitated. The flask was allowed to cool and the mixture was centrifuged. The clear liquid was stored in a 250 milliliter flask. A 10 milliliter aliquot of this portion was titrated in duplicate against 0.1 N hydrochloric acid. This procedure gave the total acidity (carboxyl and hydroxyl).

A complete flow sheet for the analysis is shown in Figure 1.

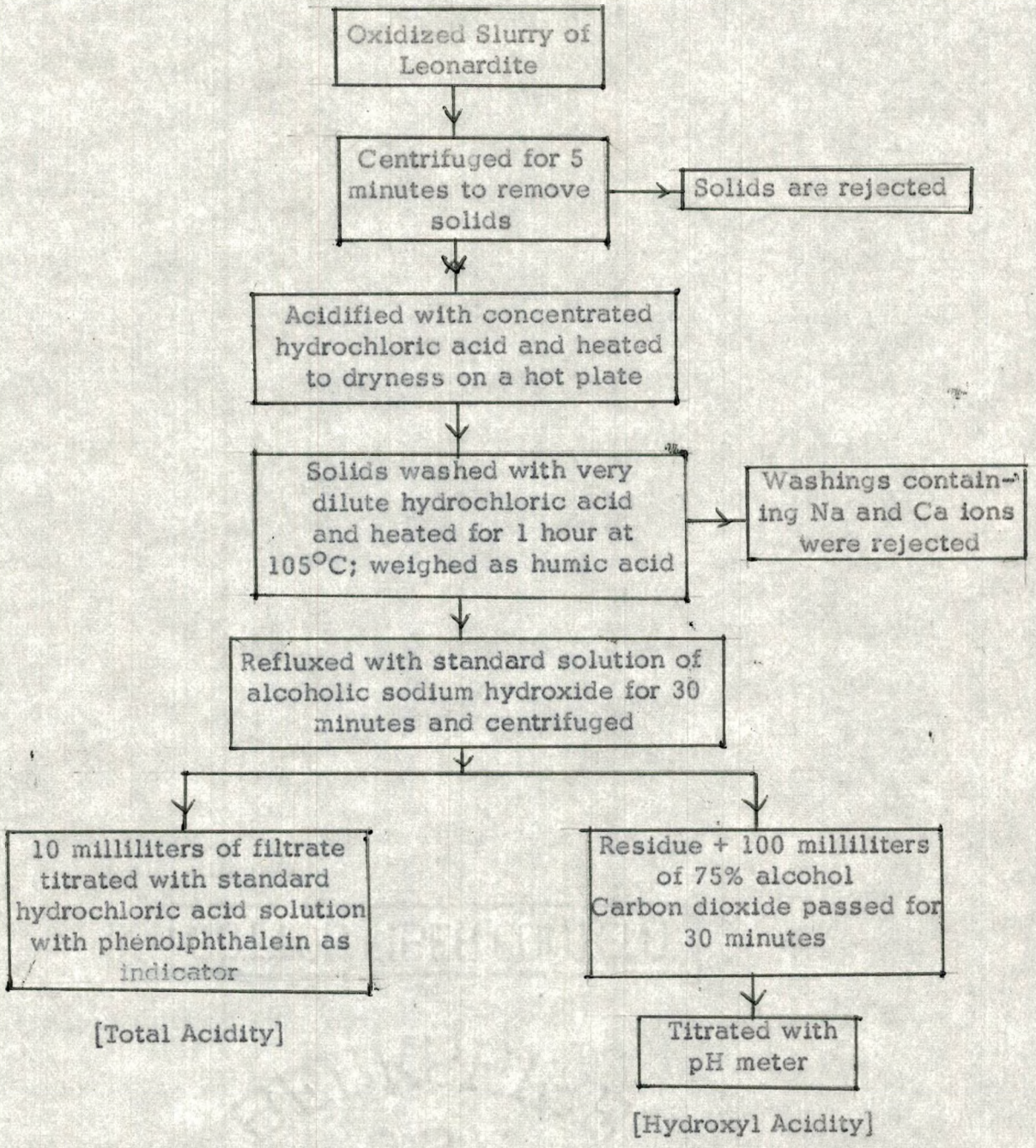
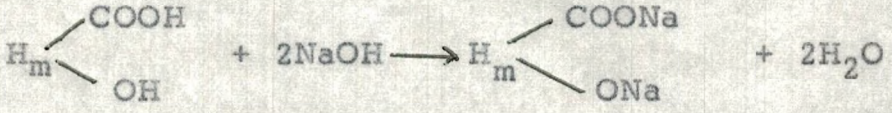


Fig. 1.--Flow Sheet for Analysis

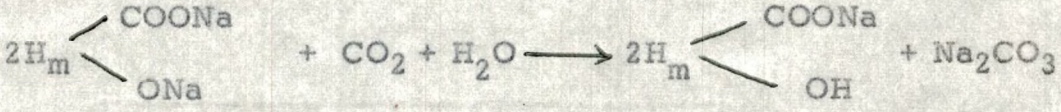
The residue from the centrifugation was dissolved in 100 ml. of 75% solution of ethanol in water. Carbon dioxide was then bubbled through the slurry for half an hour. The slurry was then centrifuged and an aliquot portion titrated to a pH of 7 with 0.1 N hydrochloric acid using a pH meter. This part of the analytical procedure gave equivalents of hydroxyl acid in a given sample.

By subtracting the hydroxyl acid from the total acidity, the carboxyl acid in a given sample of leonardite was obtained.

The reaction in the first part of the analytical procedure is as follows:



When carbon dioxide is passed through the slurry to determine the hydroxyl acid content, the following reaction takes place.



EXPERIMENTAL RESULTS

In all, sixteen runs were performed with four levels of concentrations of sodium hydroxide and four levels of temperatures. The duration of the reaction was limited to one hour and pressure was maintained at 500 psig.

The results of the experiments are presented in the following tables, which give average values for milliequivalents of acid on different bases: per gram of raw leonardite (MAF) in Table 3 and per gram of humic acid (MF) in Table 4. Complete sets of observations are tabulated in Appendix C. Detailed calculations are shown in Appendix B. In the case of unoxidized leonardite, a 2% concentration of sodium hydroxide was used for dissolving leonardite and the autoclave was pressurized to about 100 psig at room temperature for sampling slurry. The duration of stirring was 40 minutes.

The average percent yield of humic acid on the basis of raw leonardite (MAF) is given in Table 5. Complete sets of observations are listed in Appendix C.

TABLE 3

ACIDITY PER UNIT WEIGHT OF HUMIC ACID
[Milliequivalent per Gram of Humic Acid (MF)]

Unoxidized humic acid: Acidity

Carboxylic	6.20
Hydroxyl	2.15
Total	8.36

Oxidized humic acid: Acidity

NaOH Concentration in % / Temperature	Acidity	1	2	4	6	8
25°C	Carboxylic	5.22	6.55		5.67	6.17
	Hydroxyl	1.06	1.81		1.56	2.13
	Total	6.28	8.36		7.23	8.30
50°C	Carboxylic	6.50	7.02	6.24	6.56	6.27
	Hydroxyl	1.95	1.82	1.83	2.33	1.41
	Total	8.45	8.84	8.07	8.89	7.68
75°C	Carboxylic	6.01	7.09	7.02	7.38	6.74
	Hydroxyl	1.48	2.16	1.34	1.59	1.36
	Total	7.49	9.25	8.36	8.97	8.10
125°C	Carboxylic	6.20	6.72		6.61	4.71
	Hydroxyl	1.65	1.26		1.75	0.84
	Total	7.85	7.98		8.36	5.55

TABLE 4

ACIDITY PER UNIT RAW MATERIAL
[Milliequivalents per Gram of Raw Leonardite (MAF)]

Raw leonardite: Acidity

Carboxylic	5.23
Hydroxyl	1.82
Total	7.05

Oxidized products: Acidity

NaOH Concentration in %		1	2	4	6	8
Temperature	Acidity					
25°C	Carboxylic	6.20	5.98		4.76	5.10
	Hydroxyl	1.20	1.58		1.45	1.64
	Total	7.40	7.56		6.21	6.74
50°C	Carboxylic	5.55	6.03	5.05	5.95	5.06
	Hydroxyl	1.75	1.53	1.49	1.45	1.67
	Total	7.30	7.56	6.54	7.40	6.73
75°C	Carboxylic	4.88	5.69	5.78	5.15	5.50
	Hydroxyl	1.09	1.44	1.13	1.36	1.00
	Total	5.97	7.13	6.91	6.51	6.50
125°C	Carboxylic	4.92	4.68		3.44	3.12
	Hydroxyl	1.30	1.74		0.90	0.54
	Total	6.22	5.42		4.34	3.66

TABLE 5

THE AVERAGE PERCENT YIELD OF HUMIC ACID

NaOH Concentration in % / Temperature	1	2	4	6	8	Unoxidized Leonardite
25	85.3	90.25		81.8	82.7	
50	73.3	85.60	81.2	85.1	85.1	
75	80.9	76.6	82.7	72.7	82.5	83.1
125	79.4	66.6		51.6	66.1	

In Figure 2, total acidity per gram of humic acid is plotted against temperature, and in Figure 3, total carboxyl acid is plotted against temperature. In Figure 4 total acidity per gram of raw leonardite (MAF) is plotted against temperature, and in Figure 5 total carboxyl acid is plotted against temperature. In Figure 6 yield in percent is plotted against temperature, with concentration as a parameter. Figure 7 is a contour diagram showing the effect of temperature and concentration of sodium hydroxide on the total acidity per gram of humic acid.

Two runs were duplicated to determine the reproducibility of the runs. One run was carried out at 6% level of caustic concentration, and at a temperature of 25°C. The other was at the same concentration of caustic but at 50°C. Results were reproducible and the maximum error involved was 9%.

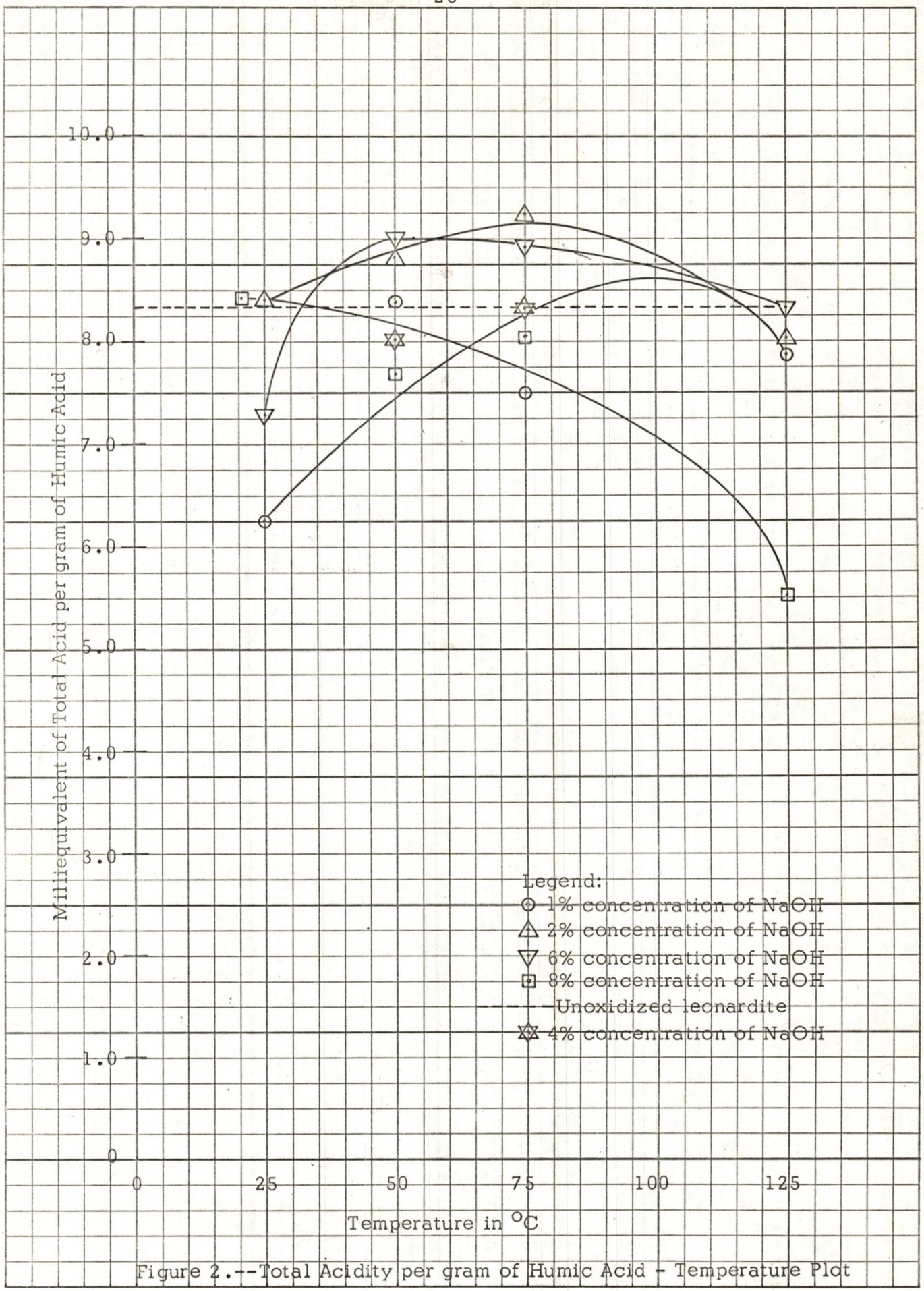


Figure 2.--Total Acidity per gram of Humic Acid - Temperature Plot

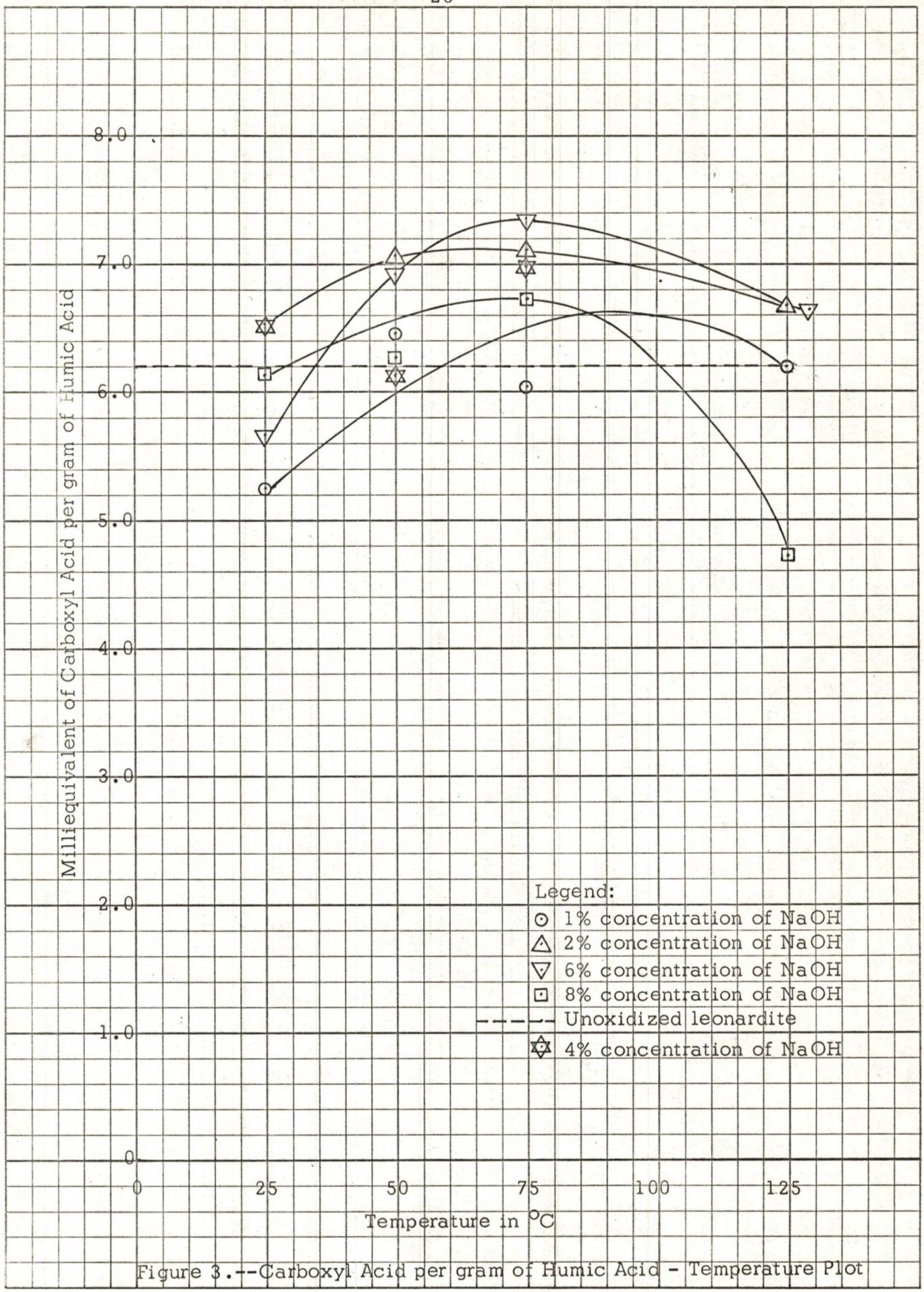


Figure 3.--Carboxyl Acid per gram of Humic Acid - Temperature Plot

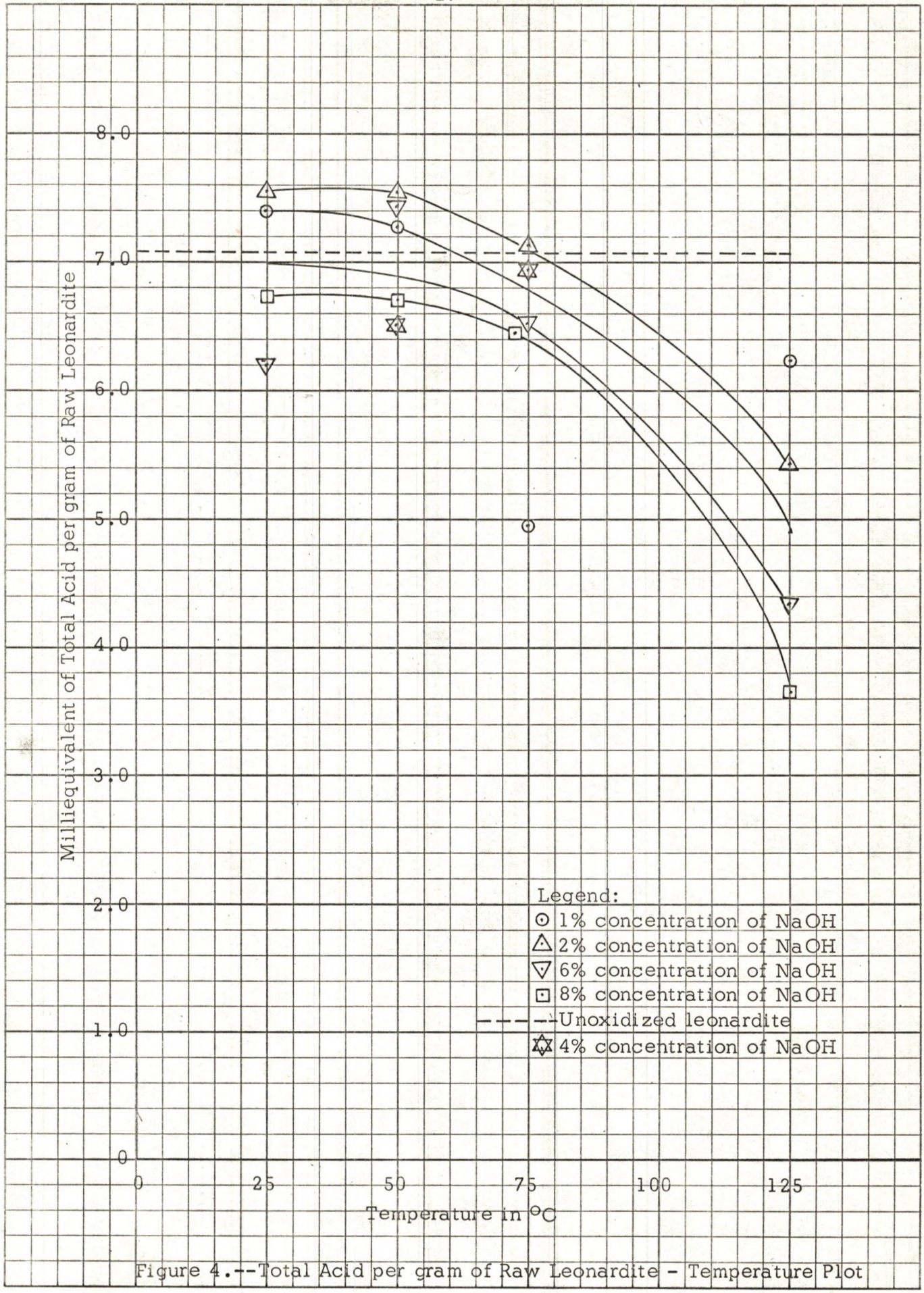


Figure 4.--Total Acid per gram of Raw Leonardite - Temperature Plot

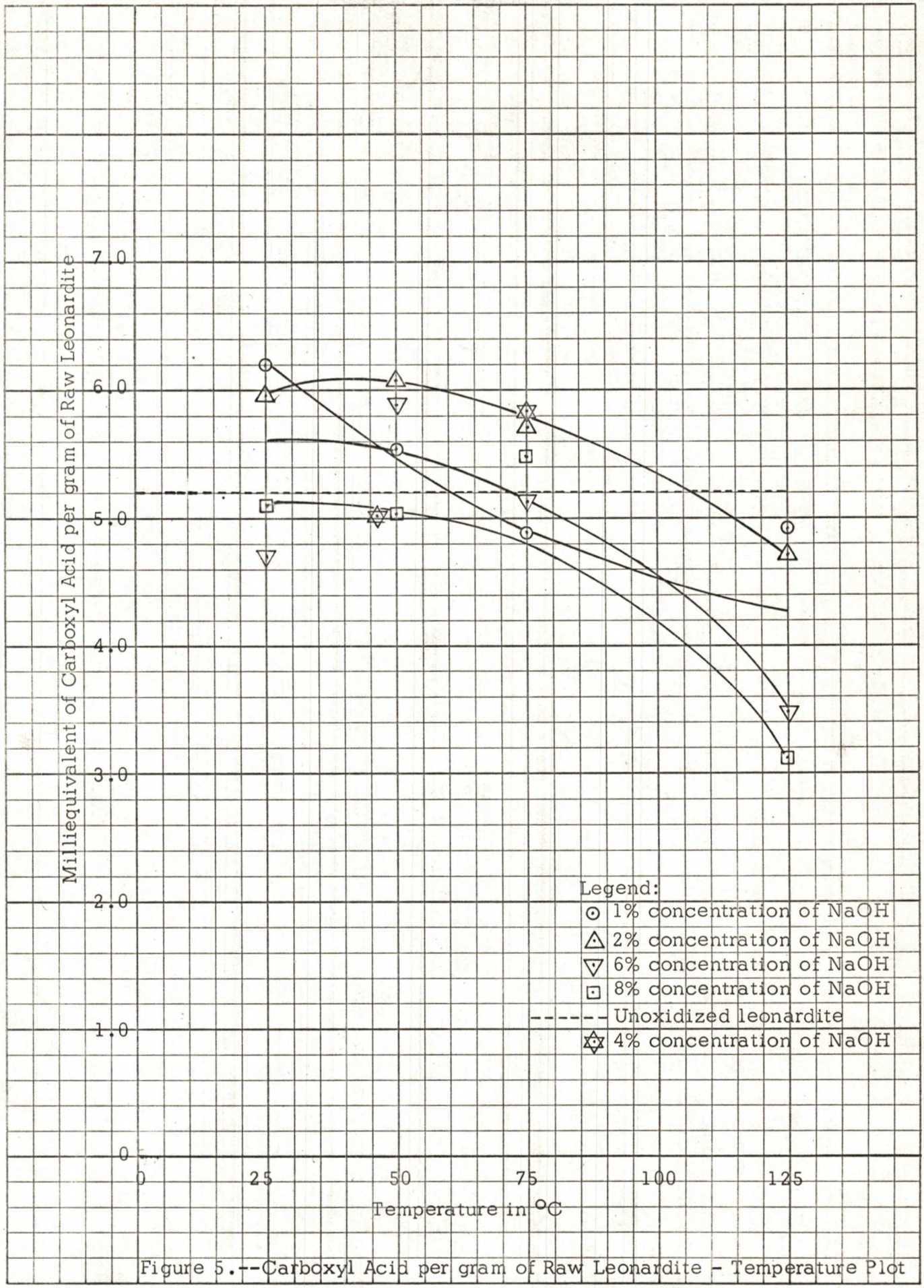


Figure 5.--Carboxyl Acid per gram of Raw Leonardite - Temperature Plot

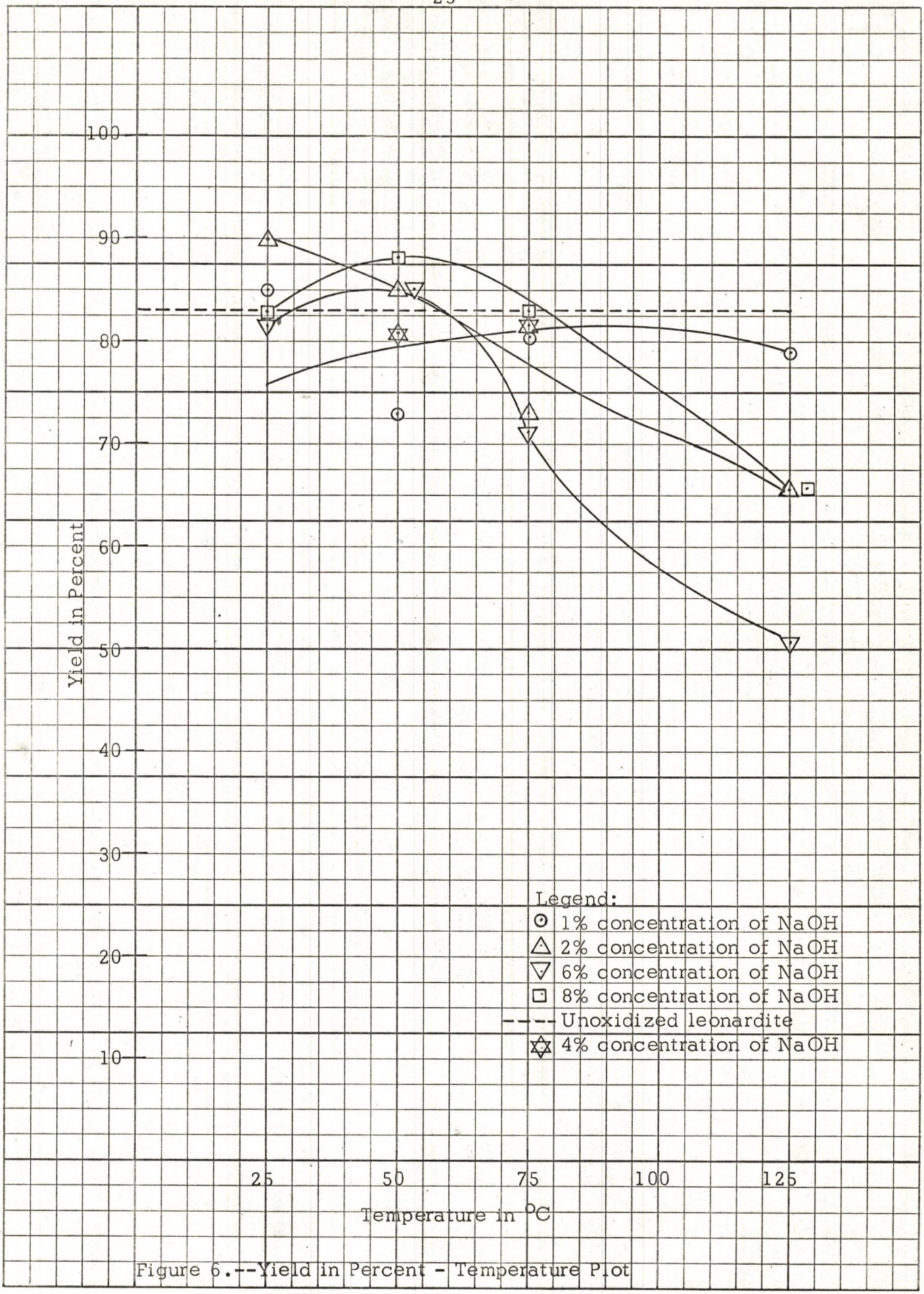


Figure 6.--Yield in Percent - Temperature Plot

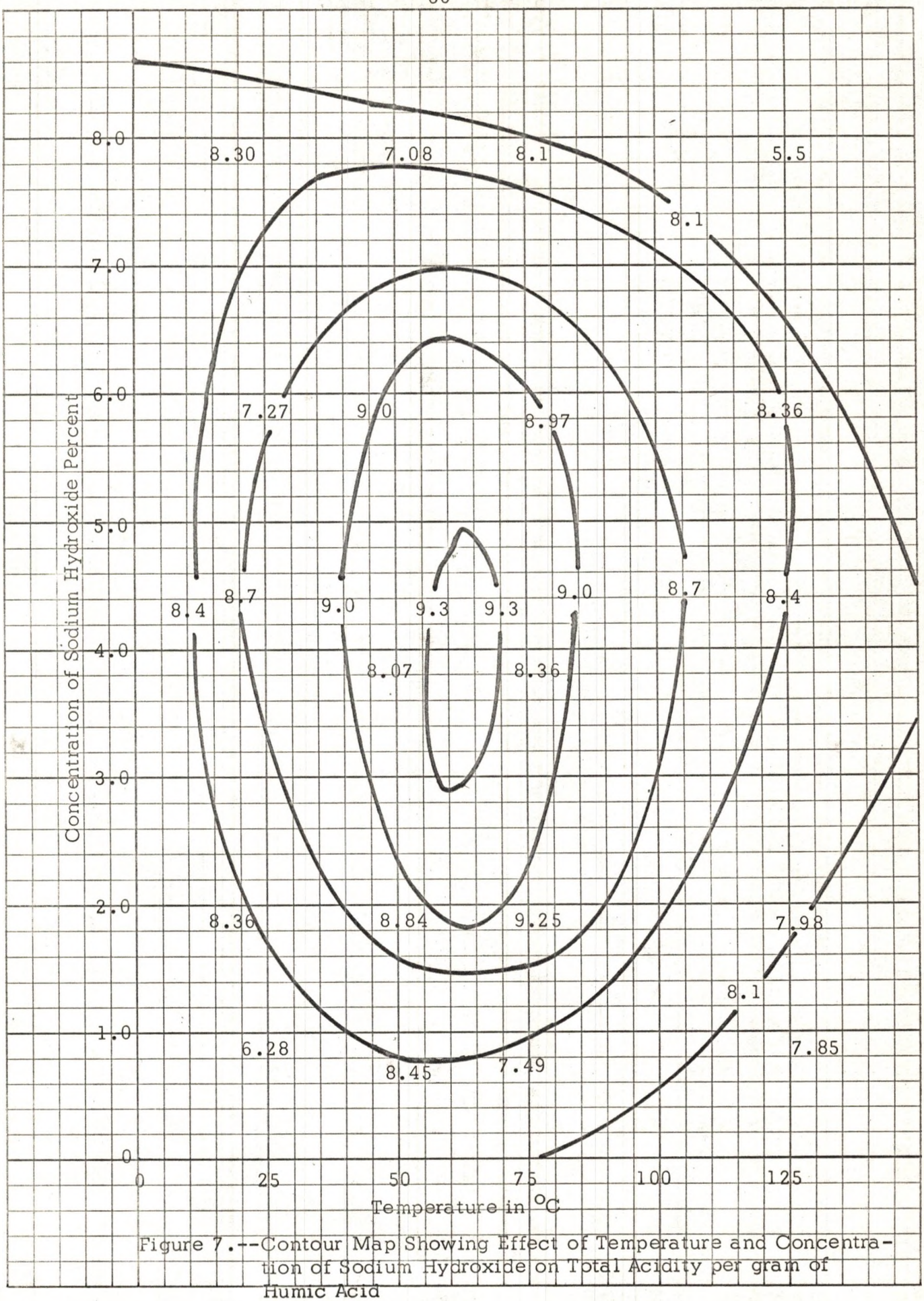


Figure 7.--Contour Map Showing Effect of Temperature and Concentration of Sodium Hydroxide on Total Acidity per gram of Humic Acid

DISCUSSION OF RESULTS

As stated earlier leonardite has a high initial oxygen content of about 30 percent(3) on m.a.f. basis, and from the experimental data it appears that it is very sensitive to further oxidation as compared to bituminous coal. Tables for the analysis of variance are shown in Appendix D.

From Table D-1 it is observed that the results are not significant at 95% confidence level; i.e. temperature and concentration do not affect the total acidity per gram of humic acid. The standard deviation is 0.875. Table D-2 shows the analysis of variance for total acidity per gram of leonardite (MAF). The concentration effect is not significant at 95% confidence level but the temperature effect is significant. The total acidity gradually decreased as the temperature of the reaction is increased. The standard deviation for total acidity per gram of leonardite is 0.780.

The standard deviation for the analytical procedure for the total acidity per gram of humic acid is 0.271 and for the total acidity per gram of raw leonardite is 0.324.

There are two types of reactions taking place, perhaps simultaneously: carboxylation at active sites in the aromatic or olefinic structures of humic

acid and decarboxylation. In certain cases, the oxidation is carried further and combustion of leonardite takes place and the yield of humic acid is reduced. In preliminary runs tabulated in Appendix E, it was found for a 20% concentration of sodium hydroxide and a temperature of 180°C and a pressure of 400 psig, the yield of humic acid was zero, in spite of the fact that the duration of oxidation was only 15 minutes. Similar results were obtained for a 5% caustic concentration at 250°C. The products of excessive oxidation are water soluble acids or carbon dioxide and water.

From Figure 2, it is seen that total acidity per gram of humic acid decreases with temperature at the 8% concentration level, and perhaps decarboxylation and combustion result above 35°C. At 125°C a substantial amount of humic acid is converted to carbon dioxide and water soluble acids. This is reflected in the low yields of humic acids in Table 5. Decarboxylation results in carbon dioxide, which is lost from the sphere of reaction as it is absorbed in the caustic solution.

$$CO_2 + 2NaOH \longrightarrow Na_2CO_3 + H_2O$$

When oxidized liquor of leonardite is acidified by hydrochloric acid to precipitate humic acid, there is effervescence due to carbon dioxide evolution.

$$Na_2CO_3 + 2HCl \longrightarrow 2NaCl + CO_2 + H_2O$$

Effervescence was observed for all the runs at 75°C and 125°C. At 2% and 6% levels of caustic concentrations there is a maximum

total acidity per gram of humic acid between 50°C and 75°C. In the case of 1% level of caustic concentration, the maximum total acidity is between 75°C and 125°C.

It is seen from Figure 3 that at 8% level of caustic concentration, there is a definite trend towards decomposition of carboxyl groups. However at 1% level, there is a slight gain in carboxyl groups with increase in temperature up to 125°C. In the case of 2% and 6% levels, carboxyl groups have a maximum value between 50°C and 75°C.

Figure 4 shows total acidity per gram of raw leonardite. This shows decomposition of humic acid molecules throughout the range of temperatures and concentrations of sodium hydroxide. Figure 5 shows total carboxyl groups per gram of raw leonardite. At 2% level of caustic concentration, there is a maximum value of carboxyl groups between 25°C and 75°C. However at 1%, 2% and 8% levels of caustic concentration, there is decomposition taking place at all the levels of temperatures.

As shown in Figure 6 at 125°C, the yields are very low, particularly for 2%, 6% and 8% levels of caustic concentrations, perhaps due to destructive oxidation of humic acids. In the case of 2% level, the yield is highest at 25°C; at the 6% and 8% level of concentration, a maximum occurs at 50°C. However for 1% level, the yield does not vary much with temperature.

On Figures 2, 4 and 6, not only the yields are lowest at 125°C for

the concentrations except 1% level, but the total acidity is also lowest. This indicates decarboxylation and combustion have dominated throughout the course of reaction. However, between 50° and 75°C and for concentration range 2% and 8%, the yield is falling, whereas the total acidity per gram of humic acid curve passes through a maximum value. This indicates perhaps that certain portion of humic acid is being selectively enriched with carboxyl groups. Furthermore part of the humic acid is being subjected to excessive oxidation to form carbon dioxide and water soluble acids.

A contour diagram is shown in Figure 7, representing temperature, concentration of sodium hydroxide and acidity in milliequivalents of acid. It is seen from this figure that maximum acidity per gram of humic acid is in the temperature range of 50°C to 75°C, and in the concentration range of 2% to 6%. Two experiments were run at 4% level with temperature at 50°C and 75°C, pressure maintained at 500 psig and time limited to one hour. However, the results of these two experiments showed that total acidity at 50°C was 8.07 milliequivalents and at 75°C was 8.36 millequivalents of acid. These two values are lower than the ones expected from the contour diagram.

There are two marked regions in the contour diagram in which the acidity is low. One region has high concentrations of caustic and high temperatures of reaction. In this region the decomposition of humic acid takes place and low yields of humic acid were obtained.

Preliminary work was done in this region. In the second region, one of low concentrations of caustic and low temperatures, the acidity is low because temperature is too low for any appreciable reaction to take place. Furthermore at low concentrations, all the leonardite will not dissolve in caustic solution.

SUMMARY

Leonardite was oxidized in aqueous solutions of sodium hydroxide of various concentrations. The other variables were temperature, pressure and the duration of oxidation. The results clearly indicate that leonardite does not react with substantial amount of oxygen to form humic acids in an aqueous medium of sodium hydroxide in the range of variable studied.

Decarboxylation and combustion at higher temperatures and higher concentrations were observed. This was particularly noticed in the case of 125°C and 8% level of concentration. The yields of humic acids were also low at 125°C.

There appeared to be an optimum concentration between 2% and 6% concentration level of sodium hydroxide and an optimum temperature between 50°C and 75°C, at which total acidity per gram of humic acid would be maximum. Two more experiments were carried out at 2% level of concentration, and at 50°C and 75°C. The pressure was maintained at 500 psig and the duration of oxidation was limited to one hour. However the results of these two experiments showed that total acidity per gram of humic acid does not increase.

RECOMMENDATIONS FOR FURTHER WORK

The Parr Reactor Series 4500 was not fitted with a cooling coil. This fact made it very difficult to run reactions at isothermal conditions. A cooling coil should be easily installed in this unit at a little cost and without lowering the present temperature and pressure ranges in order to promote easier temperature control.

No attempt was made in this project to determine the chemical structure of the humic acids. It would be worthwhile to use techniques of chromatography to separate the various aromatic structures that make up the humic acid molecule, and then to see what structural changes have occurred in the humic acid molecule during oxidation in an aqueous alkaline medium. The constituents then could be identified by infra-red and mass spectrophotometric techniques.

The use of humic acid as a binding material for taconite has already been mentioned. The oxidized form of humic acid may prove to be better material for bonding taconite and further work should be done in that direction. The oxidized form of leonardite may also prove to be a better additive in oil-well drilling mud for viscosity control and for the other uses mentioned earlier.

In this project aqueous solutions were used for dissolving

leonardite for oxidation. From the results it is quite obvious that aqueous solutions are not well suited for the controlled oxidation of leonardite to highly acidic products. Further studies on oxidation of leonardite should be carried out in non-aqueous solutions, i.e. organic solvents. However, special precautions may have to be taken as most of the organic solvents, which dissolve leonardite, are flammable.

A complete acid balance should be carried out. It would be then possible to determine how much water soluble acids are formed and how much of the acid is insoluble in sodium hydroxide after oxidation.

A complete material balance should be made to determine what fraction of leonardite is converted to carbon dioxide, which is an undesirable by-product.

APPENDIX A

PREPARATION OF SAMPLE OF LEONARDITE (2.17)

A one hundred pound sample of leonardite was obtained from the Knife River Coal Mining Company. About 70 pounds of the leonardite were crushed to minus 1/4" size. The crushed sample was then spread evenly on a canvas sheet and allowed to dry in air.

A ten pound sample of the original leonardite was weighed and separately air dried to determine air drying losses. Samples from the air dried leonardite were ground to a minus 60-mesh in a ball mill. Some coarse particles remained on the sieve. As these particles were likely to consist largely of ash-forming substances, they were reduced to minus 60-mesh size in a mortar and added to the ball-mill ground portion of leonardite. The entire mass was then mixed thoroughly and subdivided by riffling to about two pound sub samples and stored in sealed cans. Each can was considered to be a representative sample.

The moisture content of this sample was determined by the 'xylene method'.(12) The sample, which is air dried contained 15% moisture.

APPENDIX B

Sample Calculations and a typical temperature history of a run

Run No. - 4

Pressure - 500 psig

Temperature - 75°C

Time - 1 hour

Concentration of Sodium Hydroxide - 2%

Time in Minutes	Variac Reading	Temperature of Slurry in °C	Pressure in the Autoclave	Remarks
0	65	35	-	
10	40	45	-	
15	0	65	-	Oxygen supplied from the tank
30	0	74	500	
32	0	75	"	
33	"	78	"	
35	"	79	"	
37	"	80	"	
40	"	82	"	
45	"	82	"	
60	"	80	"	
75	0	76	"	
80	10	75	"	
90	10	75	500	

Complete Sample Calculation: Run No. 4

Weight of flask + slurry sample - 109.1 gms.

Weight of flask - 83.1 gms.

Weight of sample - 26.0 gms.

Weight of mixture into autoclave - 535.2 gms.

From Material Balance:

Weight of raw leonardite in the sample is given by

$$\frac{25 \times 26.0}{535.2} = 1.215 \text{ gms.}$$

Since all the calculations are on the moisture and ash free basis, the weight of leonardite is then

$$1.215 \times 0.726 \text{ gms.}$$

$$= 0.883 \text{ gms.}$$

[1 gm. of air dried leonardite has 0.274 gm. of ash and moisture]

Total amount of humic acid weighed 0.6741 gms.

yield of humic acid = 76.25%

Total amount of hydrochloric acid (0.1N) required to neutralize 10 milliliters of aliquot 7.7 ml.

Amount of hydrochloric acid required to neutralize hydroxyl groups 12.5 ml.

Total acidity (x) of the sample is then given by

$$7.7 \times 5 \times 0.1 = (50-x)\ 0.2$$

$$X = \frac{10 - 3.85}{0.2}$$

$$= 30.75 \text{ ml.} \ldots\ldots \text{(a)}$$

Hydroxyl groups are given by

$$= \frac{12.5 \times 0.1}{0.2}$$

$$= 6.25 \text{ ml.} \ldots\ldots \text{(b)}$$

Carboxylic groups are given by =[a] - [b]

$$= 30.75 - 6.25$$

$$= 24.50 \text{ ml.}$$

Total acidity per gram of raw leonardite moisture and ash free is equivalent to $\frac{30.75}{0.883}$ ml. or 34.0 ml.

Carboxylic groups are given by $\frac{24.50}{0.883}$ ml. or 28.9 ml.

Total acidity per gram of humic acid obtained is $\frac{30.75}{0.6471}$

or 45.70 ml.

Carboxylic groups are given by $\frac{24.50}{0.6741}$ or 36.4 ml.

Milli-equivalents of acid are obtained by multiplying respective volumes by normality. They are tabulated below:

Total Acidity per gram of raw leonardite (MAF)	Carboxylic groups per gram of raw leonardite (MAF)	Total Acidity per gram of humic acid obtained	Carboxylic groups per gram of humic acid obtained
6.8	5.75	9.15	7.08

APPENDIX C

DETAILED EXPERIMENTAL RESULTS

The following tables give the acidity of each run. Initially in some runs triplicates were run to determine the reproducibility of the analysis.

TABLE 1

TOTAL ACIDITY IN TERMS OF MILLIEQUIVALENT OF ACID PER GRAM OF RAW LEONARDITE (MAF)

Concentration of NaOH in % / Temperature in °C	1%	2%	4%	6%		8%	Unoxidized Leonardite
25	7.58	7.50		6.60	6.6	6.84	
	7.23	7.61		6.27	6.22	6.64	6.8
50	7.42	7.83	6.63	7.38	7.05	6.55	6.9
		7.26		7.72			
	7.18	7.59	6.45	7.86	7.00	6.92	7.04
75	6.2	6.80	6.90	6.42		6.32	
		6.84					7.30
	5.75	7.74	6.92	6.6		6.68	
125	6.15	5.36		4.30		3.52	7.25
	6.30	5.48		4.38		3.80	

TABLE 2

TOTAL CARBOXYLIC GROUPS IN TERMS OF MILLEQUIVALENT OF ACID PER GRAM OF RAW LEONARDITE

Concentration of NaOH in % / Temperature in °C	1%	2%	4%	6%		8%	Unoxidized Leonardite
25	6.16	5.57		4.84	4.95	5.1	
	6.25	6.40		4.37	4.79	5.1	5.3
50	5.48	6.15	5.13	5.5	5.05	4.76	5.1
		5.18		6.06			
	5.62	6.14	4.97	6.14	4.93	5.37	4.9
75	5.01	5.75	6.6	4.74		5.44	
		5.66		5.56		5.56	5.38
	4.75	5.48	7.45				5.05
125	4.95	4.48		3.24		2.89	
	4.90	4.88		3.64		3.34	

TABLE 3

PHENOLIC GROUPS IN TERMS OF MILLEQUIVALENT OF ACID PER GRAM OF RAW LEONARDITE (MAF)

Concentration of NaOH in % / Temperature in °C	1%	2%	4%	6%		8%	Unoxidized Leonardite
25	1.42	1.93		1.76	1.65	1.74	
	0.98	1.21		1.90	1.48	1.54	1.50
50	1.94	1.68	1.50	1.88	2.00	1.79	1.79
		1.46		1.66		1.55	
	1.50	1.45	1.48	1.72	2.07		2.14
75	1.19	1.05	1.32	1.68		0.88	1.94
		1.18					
	1.00	1.26	.94	1.04		1.12	1.93
125	1.20	0.88		1.06		0.63	
	1.40	0.60		0.74		0.46	

TABLE 4

TOTAL ACIDITY IN TERMS OF MILLIEQUIVALENT
OF ACID PER GRAMS OF HUMIC ACID
(MOISTURE FREE BASIS)

Concentration of NaOH in % / Temperature in °C	1%	2%	4%	6%		8%	Unoxidized Leonardite
25	6.56	8.27		7.60	7.55	8.40	
	6.00	8.45		6.94	6.90	8.20	7.94
50	8.58	9.06	8.0	8.6	8.72	7.47	8.5
		8.82		9.32		7.90	
	8.32	8.64	8.15	9.08	8.25		8.47
75	7.58	9.15	8.0	8.92		8.24	8.55
		8.90		9.02		7.96	
	7.40	9.70	8.72				8.35
125	7.75	8.08		8.62		5.39	
		7.66		8.10		5.70	
	7.95	7.70					

TABLE 5

TOTAL CARBOXYLIC GROUPS IN TERMS OF MILLIEQUIVALENT OF ACID PER GRAM OF HUMIC ACID

Concentration of NaOH in % / Temperature in °C	1%	2%	4%	6%		8%	Unoxidized Leonardite
25	5.34	6.20		5.84	5.70	6.22	
	5.10	6.90		5.42	5.75	6.12	6.12
50	6.64	7.14	6.2	6.54	6.05	6.45	6.32
		7.0		7.16			
	6.36	6.92	6.28	7.08	6.00	6.10	5.90
75	5.96	7.08	6.6	7.16		6.84	6.30
		7.32					
	6.07	6.88	7.45	7.60		6.64	6.36
125	6.25	6.62		6.50		4.40	
		6.74					
	6.16	6.82		6.73		5.02	

TABLE 6

PHENOLIC GROUPS IN TERMS OF MILLIEQUIVALENT OF ACID PER GRAM OF HUMIC ACID

Concentration of NaOH in % / Temperature in °C	1%	2%	4%	6%		8%	Unoxidized Leonardite
25	1.22	2.07		1.76	1.85	2.18	
	0.9	1.55		1.54	1.15	2.08	1.72
50	1.94	1.82	1.8	2.06	2.67	1.02	
		1.82		2.16			2.21
	2.06	1.72	1.87	2.00	2.75	1.80	
							2.38
75	1.62	2.07	1.4	1.76		1.40	
		1.58					2.27
	1.33	2.82	1.27	1.42		1.32	
							1.995
125	1.50	1.46		2.12		0.99	
		0.92					
	1.79	0.88		1.37		0.68	

TABLE 7

TOTAL YIELD OF HUMIC ACID ON THE BASIS OF RAW LEONARDITE (MAF)

Concentration of NaOH in % / Temperature in °C	1%	2%	4%	6%		8%	Unoxidized Leonardite
25	86.6	90.3		82.7	87.3	82.2	
	84.0	90.2		81.0	84.5	83.2	79.1
50	76.6	86.25	83.0	84.0	83	88.4	83.0
		83.0		84.75	82.40		
	70.1	87.6	79.5	86.8		87.8	87.0
75	84.2	73.6	84.5	72.0		80.1	85.5
		77.1					
	77.6	79.5	80.7	73.4		85	80.9
125	79.5	66.4		49.8		65.7	
		62.3					
	79.3	71.0		53.5		66.5	

Note: Two runs at 6% level and at 25°C and 50°C were duplicated.

APPENDIX D

STATISTICAL INTERPRETATION OF RESULTS

Since there are two sets of variables, concentration of sodium hydroxide and temperature, the experiment is considered as a two way classification. From Table 3, an analysis of variance for total acidity per gram humic acid is calculated, and from Table 4 an analysis of variance for total acidity per gram of leonardite (MAF) is calculated.

TABLE D-1

ANALYSIS OF VARIANCE FOR TOTAL ACIDITY
PER GRAM OF HUMIC ACID

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F Computed	F 0.05
Concentration of Sodium Hydroxide	6.90	3	2.30	3.01	3.86
Temperature	2.57	3	0.86	1.13	3.86
Error	6.87	9	0.763		
Total	16.34	15			

TABLE D-2

ANALYSIS OF VARIANCE FOR TOTAL ACIDITY
PER GRAM OF RAW LEONARDITE (MAF)

Source of Variation	Sum of Squares	Degrees of Freedom	Mean Square	F Computed	F 0.05
Concentration of Sodium Hydroxide	1.33	3	0.443	0.73	3.86
Temperature	7.88	3	2.626	4.32	3.86
Error	5.485	9	0.609		
Total	14.695	15			

APPENDIX E

RESULTS OF PRELIMINARY RUNS

The following table gives the results of the preliminary runs that were carried out.

Temperature in ^{o}C	Pressure psig	Time in Minutes	Concentration of NaOH in %	Milliequivalents of Total Acidity per gram of raw leonardite
100	200	15	2	6.50
100	200	15	15	5.02
100	800	20	10	7.05
200	400	15	20	Humic acids completely decomposed
150	600	15	10	5.78
200	200	10	10	7.00
150	200	25	5	5.87
250	800	15	5	Humic acids completely decomposed

This clearly indicates that humic acids decompose at higher temperatures and higher concentrations of sodium hydroxide. The pressure does not seem to have a significant effect on the total acidity per gram of raw leonardite.

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